

PRODUCTION OF SYNTHETIC ALCOHOL.

BY H. W. WILEY AND HERMAN SCHREIBER.

(Published by permission of the Acting Secretary of Agriculture.)

(Read April 20, 1907.)

When Faraday and Hennell¹ discovered that ethylene would combine with sulfuric acid, forming ethyl sulphate, a new opportunity was given for the quest of new compounds derived therefrom. The whole subsequent history of synthetic alcohol is a mass of methods and contradictions of them. Fritzsche² claims that Hennell³ first demonstrated the identity of the alcohol, made by diluting ethyl sulfate with water and distilling off the alcohol, which is plain from the above reference, while others claim that Berthelot first made this observation. Berthelot⁴ did produce alcohol from ethyl sulfate and being engaged in investigating coal gas which was known to contain ethylene he proposed that alcohol could be made from the ethylene in coal gas, but his efforts in this direction did not make its utilization appear of commercial value. However, the alcohol fever had gained a strong hold on the people, which finally lead to the offering of stock in a concern whose object was the manufacture of ethyl alcohol from coal.⁵ Cotelte, the promoter of this scheme, claimed to produce one hectoliter for 23 francs.⁶ Fritzsche⁷ states that it is doubtful that any commercial attempt was made. The chief difficulty in producing alcohol from the ethylene in coal gas at this time seemed to be the cost of reconcentrating the sulfuric acid resulting from the diluting and distilling of the ethyl sulfate. But Fritzsche claims that the enormous dilution then practiced (5-6 parts water to 1 ethyl sulfate) is not necessary and that

¹ Gmelin Krauts, "Handbook," Vol. 4, p. 721.

² *Chem. Ind.*, 1897, Vol. 20, p. 266.

³ *Philosophical Trans.* 1828 p. 365.

⁴ *Comptes rend.*, Vol. 40, p. 102.

⁵ Wagner's "Jahresbericht," 1863, p. 469.

⁶ *Chem. Ind.*, 1897, 266.

⁷ *Chem. Ind.*, 1897, 266.

dilution with an equal weight of water will give nearly the entire ethyl content as alcohol. He estimates that 95,000 hectoliters alcohol could be produced from the coal gas which is annually produced in Germany. As we do not know that alcohol is at present produced from coal gas we suppose that there are still difficulties which prevent it.

The matter has not yet lost all its interest and appears occasionally even in economic guise. Since the commercial production of calcium carbide much interest has centered in the possibility of building alcohol from it. Frazee¹ gives four possible methods of building alcohol from acetylene. The first consists in passing hydrogen and acetylene over platinum black and so gaining ethylene according to the equation $C_2H_2 + 2H = C_2H_4$ then absorbing the ethylene in sulfuric acid, diluting the ethyl sulfate and distilling off alcohol, $C_2H_4 + H_2SO_4 = C_2H_5HSO_4 : C_2H_5HSO_4 + H_2O = C_2H_5OH + H_2SO_4$. This method was not tried as Wilde² states that if hydrogen and acetylene are passed over platinum black ethane is formed and no ethylene. Frazee's second possibility is to build ethane from acetylene then make the chlorine substitution product (ethyl chlorid) and saponify this with KOH. This method would undoubtedly give alcohol but in a round about way. His third method is the building of acetaldehyde from acetylene and reduction to alcohol. This method is the best of the four which he gives and was the one by which we were finally able to make alcohol. His fourth method is the ethylene iodide method which consists in absorbing acetylene in hydriodic acid, oxidizing the ethylene iodide to acetaldehyde by means of lead oxid and then reducing the acetaldehyde to alcohol. This method has been found very difficult by Krüger and Pückert³ and was not tried by us.

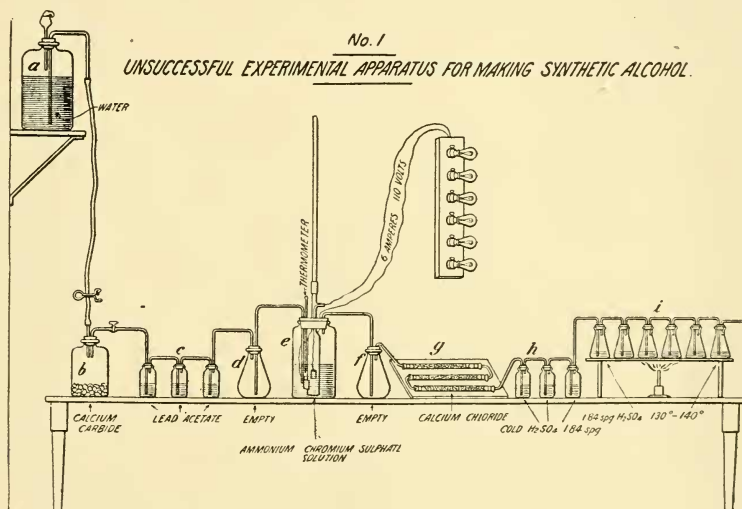
Of all the methods found by us, the one given in *The Electrical Review* (for 1899, page 375) seemed the simplest and most direct. Here the acetylene is absorbed by a solution of chromium ammonium sulfate in which hydrogen is generated electrolytically which converts the acetylene to ethylene. This ethylene passing out of the

¹ *Iowa Academy of Science*, 1904, Vol. XII., p. 179.

² *Berichte*, 7, 1874, p. 353.

³ *Chem. Ind.*, 18, 1895, p. 454.

solution is absorbed by strong sulfuric acid and forms ethyl sulfate from which alcohol is made by dilution and distillation. Apparatus No. 1 was constructed to carry out this scheme. The acetylene was generated in a two-quart Mason fruit jar (*b*). Water was fed into this jar by means of a bottle (*a*) elevated so that water siphoned from it would have a fall of six feet. The exit of the acetylene was regulated by a glass valve. The gas then passed through 3 bottles (*c*) containing lead acetate to take out sulfides, then through an empty flask (*d*) which was to take care of back pressure and then into the electrolytic cell (*e*) to be absorbed and regenerated as



ethylene, from here it passed an empty flask (*f*) to catch water which the gas might carry mechanically, then through three six-inch glass tubes (*g*) filled with calcium chloride, then three bottles (*h*) containing strong sulfuric acid (cold) to dry as thoroughly as possible and then into six flasks (*i*) containing strong sulfuric acid which was heated to 130° to 140° C. by means of a bunsen burner under the sand bath on which they stood. The current was modified by passing 6 32-c. p. lamps so that it was cut down to 6 amperes at 110 volts. This gave approximately 3 liters of hydrogen per hour and the flow of acetylene was so regulated that the quantity passing should be about 2½ liters per hour, or about 10 times

the weight of the passing hydrogen. The chromium ammonium sulfate was made acid by 10 cc. of concentrated sulfuric acid to prevent deposition on the electrodes and was kept at a temperature approximately 40° C. as directed in the method. If the six bottles (containing strong sulfuric acid) intended to absorb the ethylene were kept cold they remained colorless but if heated they became brown, then black, and finally were thick in consistency. On diluting with water and distilling this material foamed and bumped violently so that it was impossible to distil it even on great dilution if the absorption had been carried on for several days. The process was therefore run only a few days from 1-3. The sulfuric acid was then diluted and distilled. The distillate smelled strongly of sulfurous acid and somewhat of aldehyde and gave the iodoform reaction but no alcohol could be isolated by fractionation. The contents of the three bottles containing cold sulfuric acid (which was brown also) was diluted and distilled. The distillate smelled strongly of aldehyde, gave the iodoform test and formed resins with alkali but alcohol could not be fractionated from it. The process was varied by removing the calcium chloride tubes and also by not heating the sulfuric acid, but alcohol was not obtained.

Beilstein¹ states that ethylene is produced when ammonia reacts on a mixture of zinc dust and copper acetylide. Wood² says that he was unable to make any alcohol when he used this method for producing ethylene. Due to the excitable temper of copper acetylide this method was put off to be tried only as a last resort and as we reached the desired end by another method, was not tried at all.

The aldehyde method was another possible way of procedure. But here again the literature is decidedly contradictory. Lagermark and Eltekow³ state that acetylene treated with sulfuric acid sp. gr. 1.35 (45-46%) and then distilled gives crotonaldehyde. Erdmann and Kothner⁴ state that acetylene passed into a hot solution containing one volume water and two volumes sulfuric acid is converted to crotonaldehyde and that acetylene passed through a mixture of

¹ "Handbuch," 3d ed., p. 128, Vol. 1.

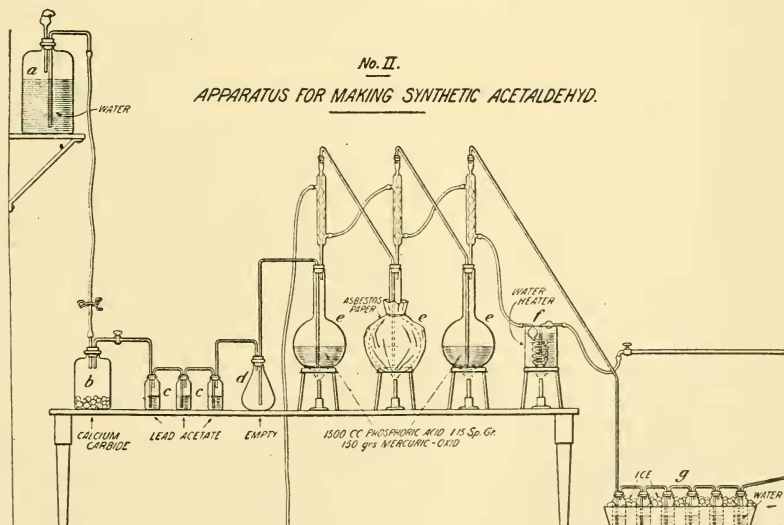
² *Chem. News*, (78), 1898, p. 308.

³ *Berichte*, 10, 637.

⁴ *Zeit. Anorg. Chem.*, 18, 1898, p. 55.

three volumes of sulfuric acid and seven volumes water is converted to acetaldehyde or that approximately 75 per cent. sulfuric acid gives crotonaldehyde, and 42 per cent. sulfuric acid gives acetaldehyde. These figures assume that Erdmann and Kothner mean H_2SO_4 1.84 sp. gr. when they say "concentrated." The latter also find that addition of mercuric oxid facilitates the process and that phosphoric acid of sp. gr. 1.15 may be used, which they claim gives a purer acetaldehyde than sulfuric acid.

Apparatus No. 2 was constructed to carry out Erdmann and Kothner's method. The acetylene was again generated in a fruit jar (*b*) and washed through lead acetate¹ (*c*) then through an empty flask (*d*) to catch any liquid forced back by back pressure. From here it passed through 3 round bottom Jena flasks (*e*) (3 liter) containing 1500 c.c. sulfuric acid (3 volumes acid, 7 volumes water) and 100 grams mercuric oxid. To prevent bumping, glass beads were put in the flasks and the flasks wound with asbestos paper. The



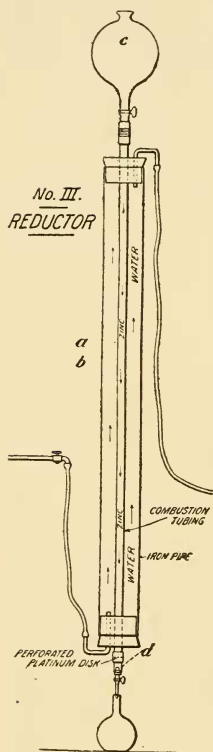
flasks rested on shallow sand baths heated by a bunsen burner. Each flask was closed by a rubber stopper carrying a reflux condenser for exit and a $\frac{3}{16}$ -inch glass tube reaching to the bottom of the flask for entry of gas. The reflux condensers were fed by warm water

¹ "Lehrbuch der anor. Chem.," Erdmann, 4th ed., p. 437.

from (f) to prevent the condensation of aldehyde as much as possible. However, the solutions soon became dark and the mercury was reduced to the metallic state where strong acid was used. The gas was run through three conversion flasks with the idea that the yield of aldehyde would be greater. The gas was now treated in various ways, sometimes washed through cold water (g) and sometimes through ammonia or sodium bisulfite. The latter ways were

abandoned as the aldehyde in a solution of ammonia or bisulfite is resinified on standing. Attempts to reduce the aqueous aldehyde by means of sodium amalgam were unsuccessful as our method of manipulation was faulty, and not according to the one devised by Wurtz.¹

The reduction of pure acetaldehyde (Kahlbaum) by passing it over palladium (precipitated on asbestos) together with hydrogen was tried but without success. Various temperatures from 20° to 400° C. were used in these experiments. Acetic acid² and zinc were not tried as the evolution of hydrogen is slow and acetaldehyde is very volatile. Acetaldehyde was diluted and attempts made to reduce it by sulfuric acid and zinc but without success as the evolution of hydrogen is slow and the process was not carried on long enough. Apparatus No. 3, a Jones reductor, was now erected consisting of a piece of combustion tubing (b) five feet long encased in a large gas pipe (a) by means of rubber stoppers and cold water circulated between the two. A separatory funnel (c) was attached



to the top of the combustion tubing by means of a rubber tube and a small perforated platinum disk formed the bottom of the tube which was extended beyond the disk by a three inch piece of the same glass tubing (d) to allow the insertion of a rubber stopper carrying a glass stopcock so that the reductor could be regulated

¹ Wurtz, *Liebigs-Annalen*, 123, p. 140.

² *Berichte*, 16, 1717 Krafft.

if necessary. The inner tube contained commercial zinc (mossy). About 25 cc. pure aldehyde were mixed with one liter dilute hydrochloric acid (four volumes acid 1.20 sp. gr. to six volumes water) and passed through the reductor until the evolution of hydrogen was very small. The zinc was then precipitated out of the resulting liquid by sodium carbonate to prevent bumping during distillation. The zinc being filtered off the filtrate was distilled. The distillate was made alkaline with caustic potash and silver nitrate added to oxidize aldehyde and after standing over night the silver was filtered off and the filtrate fractionated. The last distillation was made from an oil bath, a side necked test-tube being used as a retort. The liquid was allowed to stand over anhydrous copper sulfate before this distillation. In this way a fraction was obtained which boiled at 78° - 78.7° C. and had the odor and taste of ethyl alcohol.

Trials were also made with the reductor using zinc amalgam and sulfuric acid, and zinc amalgam and hydrochloric acid, and then using zinc and sulfuric acid, and at last zinc and hydrochloric acid which proved best. The reductor was adopted in preference to making the reduction in a bottle as the liquid in passing over the zinc was thought to give more intimate contact between the acid, aldehyde and zinc than could be obtained by means of a bottle. Aldehyde was now made by the Erdmann-Kotlner method by means of apparatus No. 2. The converters were charged with 1500 cc. phosphoric acid sp. gr. 1.15 and 150 grams mercuric oxid. The aqueous aldehyde obtained by running the apparatus 14 hours was mixed with 2 liters dilute hydrochloric acid (4 volumes acid to 6 volumes water) and the mixture passed through the reductor (apparatus No. 3) after reducing the zinc was precipitated and filtered out, the filtrate distilled and the aldehyde oxidized by silver nitrate, the filtrate from the precipitated silver was fractionated and a small fraction was obtained whose boiling point was 77.5° - 78.9° C. and which had the characteristic taste and odor of alcohol.